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This invention relates to a fluid cracking catalyst
having a high cracking activity and a high thermal and
steam stability, and to the process of preparing of this
catalyst. In one particular embodiment, this invention
relates to a low surface area silica-alumina cracking cat-
alyst prepared by an intimate admixture process as outlined in
Canadian Patent 845,705 issued June 30, 1970 to McDaniel et al which
is promoted by incorporating stabilized non-alkali aluminosilicate into
the silica-alumina matrix.

In the catalytic cracking of hydrocarbon oils, the
oil stock is vaporized by heating to a temperature of
800 to 1000°F. at greater than atmospheric pressure. The
carbon vapors are intimately contacted with silica-alumina
catalyst, wherein the high boiling constituents are con-
verted into gasoline. Several complex side reactions take
place simultaneously with the cracking reactions such as
polymerization, alkylation and the like. As a result of
these reactions, a carbonaceous deposit referred to in the
art as "coke" is formed on the catalyst. This deposit
severely impairs the cracking efficiency of the catalyst.
Catalytic activity is restored by burning the deposit from
the catalyst surface in a stream of oxidizing gas and the
catalyst is returned to the cracking process. Such regen-
eration is usually carried out at temperatures above crack-
ing temperature. The catalyst regeneration is exothermic
and excessive heat is developed during the stage of the
process.

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It is known that short life and decreasing catalytic activity is due to lack of heat and steam stability of the catalyst and occurs during the cracking process and in the regeneration stage. It is, therefore, important that the catalyst be relatively heat stable. Heat stability is particularly important in fluid cracking systems which employ finely divided solid catalysts. Thus, with the high degree of turbulence necessary in a fluid system, the catalyst undergoes physical deterioration with the

10 production of a substantial quantity of fines. These fines are difficult to retain within the system and represent a loss which often cannot be tolerated. Research to develop catalysts which have a greater mechanical strength and longer operating life is a continuing process.

There have been several attempts to prepare cracking catalysts by the co-gelation technique. However, the product of the prior art processes are fine-sized chalky materials that have high attrition losses in fluid catalytic systems and are so soft that they are readily re-

20 duced to fines in the fluid catalytic cracking system. In addition, these catalysts had very low pore volumes and surface areas.

One of the criterion of catalyst stability to steam and thermal treatment is evidenced by the loss in surface area after a standard steam or thermal treatment. Thus, a conventional silica-alumina cracking catalyst may have a surface area of about 500 M^2/g. before steam and thermal treatment and after steam and thermal treatment a surface area of only about 150 M^2/g. After this initial drop in

30 surface area, the catalyst is in an "equilibrium" state

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and retains the equilibrium surface area for the balance
of the useful catalyst life.

We have found that a catalyst having a suitable
attrition resistance can be prepared by an intimate ad-
mixture technique by careful control of reactant ratios
and reaction conditions as is set forth in our previously
referred to patent.   The catalyst prepared
according to that patent has a surface area lower
than the fresh surface area of the catalyst preopared by

10 other techniques, but is much more stable to steam and
thermal treatment. Thus, on steam treatment, the catalyst
does not lose the high proportion of surface area, and
hence activity that is typical of the conventional silica-
alumina cracking catalyst.

The catalysts prepared in accordance with the afore-
mentioned patent   have surface areas of about 250 to
350 M^2/g. and lose very little of this surface area on
steam treatment.

In our process, the necessity for adding a large

20 quantity of acid solution to the silicate solution which
would be required to gel the silicate is eliminated by
the addition of an alum solution to the sodium silicate.
Thus, by careful control of the mixing of the alum and
silicate solutions, gelation of the silicate by acids is
unnecessary.

The products produced by the process of this inven-
tion have a greatly improved initial activity as compared
with the unpromoted silica-alumina catalysts and at the
same time retain the thermal and steam stability of the

30 unpromoted intimate admixture catalysts.

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It is particularly noted here that another of the
novel aspects of the invention is the use of a _stabilized_
non-alkali metal aluminosilicate, as contrasted with the
use of alkali metal aluminosilicates typified by the prior
art processes. The prior processes thus require additional
ion exchange steps with a non-alkali metal cation to re-
move the deleterious alkali metal ion after the alumino-
silicate has been dispersed within the gel mixture. This,
of course, necessitates additional process time, cost and
10 introduces another opportunity for catalyst contamination.
The prior art has not sought to eliminate this problem in
the manner disclosed herein as among other reasons it had
always been thought, and which was true in most cases, that
the non-alkali metals were unsuitable either because they
still contained an undesirable amount of alkali ion (usually
sodium ion) or because non-alkali ion exchange with a metal
(usually a rare earth) was reversible. Thus, a large por-
tion of the non-alkali metal cation would be lost by re-
exchange with other undesirable cations in the process of
20 the catalyst manufacture. As most of these cations were
rare earth metals, their loss as well as necessitating an
additional re-ion exchange step would be quite costly.
It has been found that the use of so-called "stabilized"
non-alkali metal aluminosilicates (which have a very low
alkali metal content, in the order of 0.3 to 0.4 percent,
and which have been found not to exhibit tendency to re-
exchange with any undesirable ions which may be present
in the solutions used in the catalyst preparation) pre-
cludes the use of the addition of cation exchange steps
30 required in the prior art processes without any of the

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disadvantages thought inherent by the prior art to the use of non-alkali metal aluminosilicates.

The stabilized non-alkali metal aluminosilicates which may be used in the novel process disclosed herein are typified by the formula:

$$XM_{2/n}:0:Al_2O_3:2-7:SiO_2:yH_2O$$
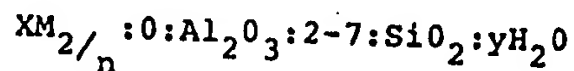
where M represents H^+ or any other cation except the alkali metals and n is its valence, where Y can vary from 0 to 9 and X from 0 to 1. Suitable cations include magnesium, maganese, zinc, thorium, aluminum, etc., and more particularly the rare earths. A more complete discussion of stabilized aluminosilicates can be found in Canadian Patent 845,705 issued June 30, 1970 to McDaniel et al.

In carrying out the process of our invention, there is first provided a 1 to 15 percent by weight SiO_2, preferably about 5.5 percent, aqueous alkali silicate solution maintained at a temperature between 70-150°F., preferably 75 to 100°F. Although any of the alkali metal silicates may be used for this solution, sodium silicate will be generally used as it is less costly. Therefore, for the purpose of simplicity, the invention will be described with respect to sodium silicate solution, unless otherwise stated.

An alum solution having a Al_2O_3 concentration of 10 to 90 grams per liter, depending upon the amount of Al_2O_3 desired in the catalyst matrix, is prepared by dissolving the appropriate amount of $Al_2O(SO_4)_3 \cdot 18H_2O$ in water. It has also been found that pore volume and surface area may be adjusted by varying the concentrations, flow rates, and temperatures of the reactant solutions

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within the ranges set forth above.

The two solutions are then mixed in a suitable mixing chamber by flowing the two solutions together in a flow ratio of about from 0.10 to 1.0, preferably 0.25, gallons of alum solution per minute per gallon of silicate solution per minute. An intimate admixture of gel-like properties is observed to form immediately upon the mixing of the solutions. The mixed solutions are then recirculated for about 15 minutes, the mixed solutions,

10 now a slurry, have a pH of about 3.0 to 4.5, dependent upon the particular alkali metal silicate solution used and the concentration of the alum solution.

After the slurry has been recirculated, the pH is brought up to a pH above 7.0, preferably from about 7.1 to 8.0 by the addition of 14 percent ammonium hydroxide. At this time, a sufficient amount of stabilized non-alkali metal aluminosilicate to yield the concentration desired in the catalyst is added to the slurry. The slurry is then aged to assure essentially complete distribution of alumino-

20 silicate. The addition of the stabilized aluminosilicate may, and usually does, result in a drop in the pH of the slurry, sufficient 14 percent ammonium hydroxide is then added to bring the solution to about the same pH it had before the addition of the stabilized aluminosilicate, i.e. above 7.0. The slurry is then filtered and reslurried with water to a solids content of 5 to 20 percent. The slurry is then spray dried and the resulting catalyst solid washed.

The washing may be accomplished by successive wash-

30 ings and filtrations of the catalyst with a dilute

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$(NH_4)_2SO_4$ solution, preferably about 4 percent by weight, followed by a second washing with a NH_4OH solution, preferably about pH 9.0, followed by a final washing with water. The catalyst is filtered after each washing and dried after the final filtration, preferably at about 400°F.

Quite obviously the particular process steps are subject to variation and modification; for example, the stabilized zeolite could be added to any nearly neutral or basic solution or slurry prior to spray drying. How-

10 ever, it is believed that the optimum point for this addition is as noted in the above description. Also, the process could be carried out continuously or batchwise, or as a combination of the two.

The invention is further illustrated by, but not in anyway limited to, the following examples.

EXAMPLE I

This example illustrates the process invention of preparing the inventive catalysts. In this particular embodiment, the intimate admixture temperature was 75°F.

20 and the catalyst produced had a 13 percent by weight Al_2O_3 matrix and contained 5 percent by weight of a rare earth aluminosilicate having a silica to alumina ratio of 2 to 3.

An alum solution was made by dissolving 3,075 grams of reagent grade $Al_2(SO_4)_3 : 18H_2O$ in enough water to make 14.2 liters of a solution having 34.8 grams of Al_2O_3 per liter. This solution was then mixed at a temperature of 75°F. and at a rate of 0.25 g.p.m. into a mixing chamber together with 1.0 g.p.m. of a 5.5 percent by weight SiO_2

30 sodium silicate solution (temperature 75°F.) for 13.5

minutes to form an intimate admixture.

The mixed solutions, now a slurry, were then aged for 15 minutes by recirculation. 600 ml. of 14 percent NH_4OH were then added bringing the pH up from 4.15 to 8.4. At this time, 258 grams of the aluminosilicate were added dropping the pH to 8.15.

The slurry was then filtered and then reslurried to a 9.3 percent solids content. This reslurry was then spray dried using a tank pressure of 50 p.s.i.g., an

10 atomizing air pressure of 35 p.s.i.g., an inlet temperature of 600°F. and an outlet temperature of 225°F.

The catalyst was then washed, maintaining a wash volume to catalyst volume of 2, five times with 4 liters each of 4 percent by weight $NH_4(SO_4)_2$ solution at 140°F., then washed three times with 4 liters of pH 9, NH_4OH solution at 140°F. and finally washed with 4 liters of water at 140°F. The catalyst was filtered after each washing.

The catalyst was then dried in a forced draft oven

20 at 400°F. for four hours.

EXAMPLE II

The catalyst prepared in this example had a 13 percent by weight Al_2O_3 matrix and contained 7 percent by weight of a rare earth aluminosilicate having a silica to alumina ratio of greater than 3 to 7. The intimate co-precipitation temperature was 75°F.

The alum solution and silicate solution were pre-pared, mixed together for 14.25 minutes, and aged in the same manner as in Example I. After aging 1.05 liters of

30 14 percent NH_4OH were added bringing the pH from 4.0 to

7.75. 278 grams of the aluminosilicate were then added
followed by the addition of 50 ml. of 14 percent NH_4OH
solution bringing the pH from 7.0 to 7.5. The slurry
was then filtered and reslurried with water to a solids
content of 11 percent.

The reslurry was then spray dried, washed, and
dried in the same manner as in Example I.

EXAMPLE III

The catalyst prepared in this example had a 13

10   percent by weight Al_2O_3 matrix and contained 7.3 percent
by weight of a rare earth aluminosilicate having a silica
to alumina ratio of 2 to 3. The intimate co-precipitation
temperature was 100°F.

The alum solution and silicate solution were pre-
pared, mixed together for 15 minutes, and aged in the
same manner as in Example I with the exception that the
temperature of the silicate solution and alum solutions
were respectively 100°F. and 102°F. After aging, 900 ml.
of 14 percent NH_4OH were added to the slurry raising the

20   pH from 4.2 to 8.2. 442 grams of the aluminosilicate were
then added followed by the addition of 60 ml. of 14 percent
NH_4OH bringing the pH from 6.6 to 7.85. The slurry was
then filtered and reslurried with water to a solids con-
tent of 12.1 percent solids content.

The reslurry was then spray dried, washed, and dried
in the same manner as Example I.

EXAMPLE IV

The catalyst prepared in this example had a 25 per-
cent Al_2O_3 matrix and contained 7 percent by weight of a

30   rare earth aluminosilicate having a silica to alumina ratio

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of greater than 3 to 7. The temperature of intimate co-precipitation was 7⁻°F.

An alum solution was made by dissolving 6,805 grams of reagent grade $Al_2(SO_4)_3 \cdot 18H_2O$ in enough water to make 14.2 liters of a solution having 77.2 grams of Al_2O_3 per liter. The solutions were then mixed for 15 minutes and aged in the same manner as in Example I. After aging 5.6 liters of 14 percent NH_4OH were added raising the pH from 3.5 to 7.6. 342 grams of the aluminosilicate were

10 then added and the slurry aged for 5 minutes. 200 ml. of 14 percent NH_4OH solution were then added bringing the pH of the slurry to 7.65. The slurry was then filtered and reslurried to a solids content of 11.7%.

The reslurry was then spray dried, washed, and dried in the same manner as Example I.

EXAMPLE V

The catalyst prepared in this example had a 25 percent Al_2O_3 matric and contained 7 percent by weight of a rare earth aluminosilicate having a silica to alumina ratio

20 of 2 to 3. The intimate co-precipitation temperature was 75°F.

The alum solution and silica solution were prepared, mixed, and aged in the same manner as Example IV. After aging 5.6 liters of 14 percent NH_4OH solution were added raising the pH from 3.5 to 7.4. 490 grams of the alumino-silicate were then added followed by the addition of 300 ml. of 14 percent NH_4OH bringing the pH from 6.9 to 7.5.

The slurry was then filtered, reslurried, spray dried, washed, and dried in the same manner as Example IV.

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It is here noted that the weight percent of aluminosilicate in the catalyst, both in the specification and claims, is determined by multiplying the $Al_2O_3:SiO_2$ content of the aluminosilicate (and not the total weight of the aluminosilicate) by 100 and then dividing by the total weight of the catalyst.

The respective surface areas and pore volumes of the catalysts produced in the examples after being calcined for three hours at 1000°F. were determined by the conventional Brunauer-Emmett-Teller method using nitrogen. The results of these determinations are summarized in Table I.

<div align="center">

Table I

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Example No.	%Al_2O_3 Matrix	T°F. of Reaction	Surface Area M^2/g.	Pore Volume cc./g.
1	13	75	258	0.47
2	13	75	142	0.34
* 3	13	100	358	0.61
4	25	75	212	0.89
* 5	25	75	256	0.93

Examples 3 and 5 were selected as representative of this catalyst and the following tests run on these examples and the results compared with the results of the same tests run on a conventional unpromoted high surface area silica-alumina catalyst (Al_2O_3 content 25-30%).

Test I - Steam Deactivation

In this test, the samples were subjected to 100% steam at 1225°F. for 20 hours followed by another steam treatment with 20% steam, 80% air at 1520°F. and the re-

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spective surface areas and pore volumes measured after each treatment.

Test II

In this test, the respective cracking properties of the catalysts after the 1520°F., 20 percent steam de-activation were determined and compared with a conventional silica-alumina catalyst having a high alumina content of 25 percent to 30 percent, nominally 27 percent.

Evaluation was made in a fixed fluidized bed cracking
10 unit utilizing a West Texas heavy gas oil feed. In each run a catalyst to oil weight ratio of 4.0 was used. The unit was operated at 920°F. with a weight hourly space velocity of 10 with no recycle.

The results of these tests I and II are summarized in Tables II and III respectively.

Table II
Catalyst Stabilities

Type Catalyst	Si_2O_3/Al_2O_3	Example III	Example V
1225°F. 100% Steam			
Surface Area M^2/g.	300	155	127
Pore Volume cc./g.	0.6	0.38	0.30
1520°F. 20% Steam			
Surface Area M^2/g.	140	79	79
Pore Volume	0.47	0.25	0.18

20

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Table III

Cracking Activity

Type Catalyst	Si_2O_3/Al_2O_3	Example III	Example V
Conversion Vol.%	52.0	59.0	60.5
Hydrogen Wt. %	0.040	0.051	0.047
C_5+ Gasoline Vol.%	44.5	51.0	51.5
Coke Wt. %	3.0	2.6	3.0

From these tables, it may be seen that even though
10 the catalysts of the examples have a lower surface area
and pore volume both before and after the steam deacti-
vation than the conventional high alumina, silica-alumina
catalyst, that these catalysts have higher conversion
rates and further higher volume conversion of the crude
oil into the desired C_5+ gasoline with no increase in the
amount of the undesired coke. Thus, it is quite apparent
that these catalysts represent a substantial improvement
over the conventional high alumina catalysts of the prior
art.

20 Obviously many modifications and variations may be
made without departing from the essence and scope of the
invention and only such limitations should be applied as
are indicated in the claims.

WHAT IS CLAIMED IS:

1. A process of preparing an aluminosilicate promoted low surface area silica-alumina cracking catalyst containing 5 to 35 percent by weight Al_2O_3 and 2 to 10 percent by weight of a stabilized aluminosilicate having the formula:

$$XM_{2/n}O:Al_2O_3:2-7SiO_2yH_2O$$
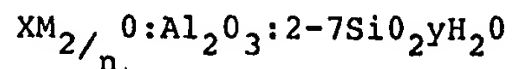
where M represents H^+ or any other cation except the alkali metals and n is its valence, where X can vary from 0 to 1 and y from 0 to 9, comprising:

(a) Preparing a 1 to 15 percent alkali metal silicate solution.

(b) Preparing an alum solution having a Al_2O_3 concentration of 10 to 90 grams per liter depending upon the Al_2O_3 desired in the catalyst.

(c) Continuously mixing the two solutions at a temperature of from 70-150°F. and at a flow rate ratio of 0.10 to 1.0 gallons of alum solution per 1.0 gallons of silicate solution, whereby a silica-alumina intimate admixture is formed.

(d) Recirculating the silica-alumina admixture solution to form a slurry.

(e) Admixing dilute NH_4OH solution to the slurry to bring the slurry to a pH above 7.0.

(f) Filtering the catalyst and reslurrying with water to a solids content of 10-20 percent by weight.

(g) Spray drying the catalyst.

(h) Washing the catalyst.

(i) Drying the catalyst.

(j)   Adding said stabilized aluminosilicate in an
amount sufficient to provide the aluminosilicate com-
position desired in the product followed by the addi-
tion of sufficient dilute ammonia hydroxide solution
to bring the pH above 7, to any basic or neutral solu-
tion or slurry in the above recited process prior to
the spray drying.

2. The process of Claim 1 wherein the addition of the stabilized aluminosilicate and the subsequent addition of dilute ammonium hydroxide takes place immediately after the first addition of ammonium hydroxide (step e).

3. The process of Claim 2 wherein the aluminosilicate is represented by the formula

$$XM_{2/n}O:Al_2O_3:3.5\text{-}7SiO_2:yH_2O$$
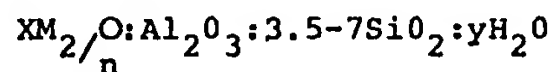
4. The process of Claim 2 wherein the aluminosilicate is represented by the formula

$$XM_{2/n}O:Al_2O_3:2\text{-}3SiO_2:yH_2O$$
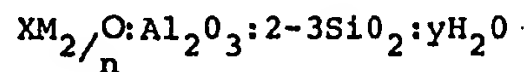
and where M is a cation of a rare earth metal.

5. An improved aluminosilicate promoted hydrocarbon fluid catalyst having a low surface area matrix of intimate co-precipitant silica-alumina, said catalyst consisting essentially of 5 to 35 percent by weight Al_2O_3 and 2 to 10 percent by weight (based on $Al_2O_3:SiO_2$ content of the aluminosilicate) of a stabilized aluminosilicate having the formula:
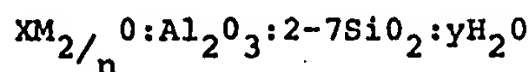
$$XM_{2/n}O:Al_2O_3:2\text{-}7SiO_2:yH_2O$$

where M represents H^+ or any other cation except the alkali metals and n is its valence, where X can vary from 0 to 1 and y from 0 to 9, dispersed within the matrix and the remainder of the catalyst being essentially SiO_2 hydrate.

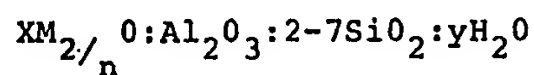6. The catalyst of Claim 5 wherein the aluminosilicate has:

$$SiO_2:Al_2O_3 \text{ ratio of 2 to 3}$$
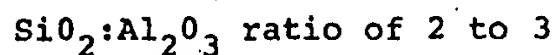
7. The catalyst of Claim 6 wherein M is a cation of a rare earth metal.

8. The catalyst of Claim 5 wherein the aluminosilicate has a SiO_2 to Al_2O_3 of 3 to 7.

9. The catalyst of Claim 8 wherein M is a cation of a rare earth metal.

10. A process for catalytic cracking of high boiling hydrocarbons to produce gas, gasoline and a middle oil distillate comprising contacting the high boiling hydrocarbons at a temperature above 850°F. with an aluminosilicate promoted silica-alumina co-precipitant catalyst consisting essentially of 5 to 35 percent by weight Al_2O_3 and 2 to 10 percent by weight of a stabilized aluminosilicate having the formula:

$$XM_{2/n}O:Al_2O_3:2-7SiO_2:yH_2O$$

where M represents H^+ or any other cation except the alkali metals and n is its valence, where X can vary from 0 to 1 and y from 0 to 9, dispersed within the matrix and the remainder of the catalyst being essentially SiO_2.